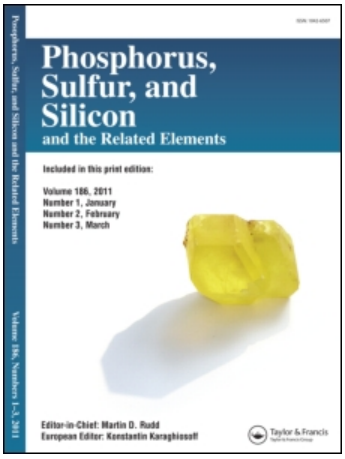

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Regeneration of Carbonyl Compounds from Phenylhydrazones Under Microwave Irradiation

Majid M. Heravi[a]; Mahmood Tajbakhsh[b]; Setareh Habibzadeh[b]; Mitra Ghassemzadeh[c]
[a] Department of Chemistry, School of Sciences, Azzahra University, Tehran, Iran [b] Department of Chemistry, University of Mazandaran, Babolsar, Iran [c] Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran

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REGENERATION OF CARBONYL COMPOUNDS FROM PHENYLHYDRAZONES UNDER MICROWAVE IRRADIATION

Majid M. Heravi,[a] *Mahmood Tajbakhsh,*[b] *Setareh Habibzadeh,*[b] *and Mitra Ghassemzadeh*[c]
Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran;[a] *Department of Chemistry, University of Mazandaran, Babolsar, Iran;*[b] *and Chemistry and Chemical Engineering Research Center of Iran, Tehran, Iran*[c]

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An environmentally benign, efficient, and mild methodology for the cleavage of phenylhydrazones using potassium ferrate under microwave irradiation in solvent-free conditions is described.

Keywords: Carbonyl compounds; microwave irradiation; phenylhydrazones; potassium ferrate; solventless system

Protection and subsequent deprotection of a functional group is almost inevitable in multistage organic synthesis.[1] Phenylhydrazones serve as important synthetic intermediates and they can be preferably used for isolation, purification and characterization of aldehydes and ketones.[2] Developing mild, efficient, ecofriendly and selective cleavage of phenylhydrazones continues to be a significant aspect of organic chemical transformation.

There has been considerable attention in the creation and development of ever green and solventless methods[3] in organic methodology dictated by stringent environment protection laws.[4] Organic solvents are not only expensive but are often flammable, toxic and environmentally hazardous. Microwave irradiation in organic synthesis is a useful technique nowadays.[5–7] Dry media using microwave thermolysis have attracted much attention, because it omits the use of hazardous and

Address correspondence to M. M. Heravi, Department of Chemistry, Tarbiat Modarres University, P.O. Box 14115-175, Tehran, Iran. E-mail: mmheravi@azzahra.ac.it

relatively expensive organic solvents and the reaction can be conducted in open vessels.[8]

Potassium ferrate (K_2FeO_4) is a sixvalent iron compound which can be easily and economically prepared by oxidizing ferric nitrate with sodium hypochlorite and the subsequent treatment with potassium hydroxide.[9] It has been recently used by P. Laszlo and his coworker for oxidizing organic substrates in nonaqueous media.[10]

Reagents adsorbed on mineral supports have gained popularity in organic synthesis due to their selectivity, ease of manipulation[11,12] and especially make them suitable and safe to be placed in a microwave oven.[13]

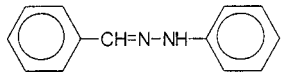
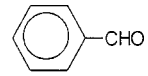
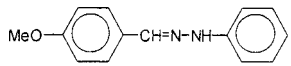
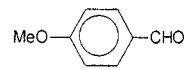
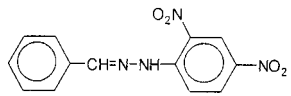
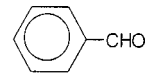
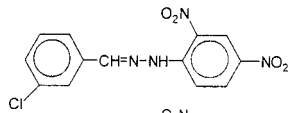
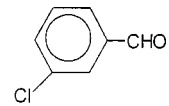
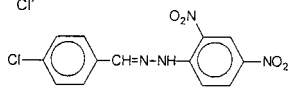
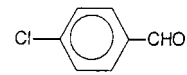
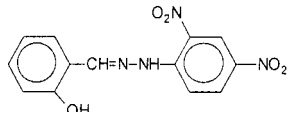
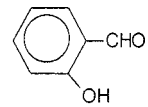
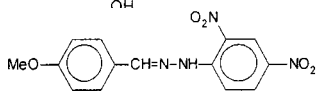
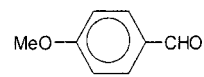
Association of ferric salts with zeolite[14–16] and clay[17] and conduction of their reactions under microwave irradiation in solvent free conditions had been pioneered in our laboratory. Armed with these experiences in this communication we wish to report that clay supported potassium ferrate can efficiently and rapidly cleave phenylhydrazones under microwave irradiation in a solventless system.

As illustrated in Table I regeneration of carbonyl compounds from their diphenyl-hydrazones was performed by mixing substrate and supported reagent with the ratio 1:3 and irradiation under microwave.

It is noteworthy to mention that in the absence of clay the reactions remain incomplete even with higher ratio of reagent (1:5) and even longer reaction time. Most seriously in the absence of clay the molten ferric salt adhered to the walls of the vessel, making the work up cumbersome. However, the reactions proceed efficiently and rapidly when potassium ferrate is mixed with equivalent weights of montmorillonite K-10. The work up procedure involves addition of solvent, mere filtration and evaporation of the solvent to afford a pure product in high yield.

In conclusion the use of nontoxic potassium ferrate permits the regeneration of carbonyl compounds from their hydrazones. The advantages of this method are mild, eco-friendly conditions, short reaction time, easy work up and high yields. We believe this procedure will find its place in organic methodology. The only drawback of this method is that the yields of the reaction for nonbenzylic derivatives are low. Potassium ferrate was prepared according to a modified procedure and supported onto montmorillonite K-10.[10] All substrates were synthesized by a known literature procedure. All products were known compounds and characterized by comparison of their physical and spectroscopic data with those of authentic samples.

TABLE I Oxidative Cleavage of Phenylhydrazones Using Potassium Ferrate Under Microwave Irradiation in Solvent-Free Conditions

Entry	Substrate[a]	Product[b]	Reaction time (min)	Yield[c] (%)
1			8	92
2			6	94
3			11	87
4			8	90
5			10	89
6			10	85
7			8	87

[a]All substrates were synthesized according to reported procedures.
[b]All products were known compounds.
[c]Yields refer to isolated products.

REGENERATION OF CARBONYL COMPOUNDS FROM THEIR PHENYLHYDRAZONES

General Procedure

A mixture of an appropriate phenylhydrazone (1 mmol) and clay supported potassium ferrate were mixed intimately in a pyrex beaker. The beaker was then placed in a household microwave oven and irradiated at an output of 900W. The progress of the reaction was monitored by TLC using pet ether-ethyl acetate 8:2 as eluent. After completion of the reaction, CH_2Cl_2 (5 mL) was added and the residue was filtered off. The organic solvent was evaporated to dryness to afford the corresponding carbonyl compound (Table I).

Caution

Although the reactions were smooth and safe in our hands, precaution for using a microwave oven is advised. It is recommended to use the microwave oven in an efficient and standard hood.

REFERENCES

[1] T. W. Green and P. G. M. Wuts, *Protective Groups in Organic Synthesis* (John Wiley, New York, 1991), 2nd ed.
[2] S. R. Sander and W. Karo, *Organic Functional Groups Preparation* (Academic Press, London, 1989), 2nd ed, vol. 3.
[3] K. Tanaka and F. Toda, *Chem. Rev.*, **100,** 1025 (2000).
[4] C. B. Khouv, C. B. Darth, J. A. Lalenger, and M. E. Davis, *J. Catal.*, **149,** 195 (1994).
[5] S. Caddick, *Tetrahedron* **38,** 10403 (1995).
[6] R. A. Abramovitch, *Org. Prep. Proceed. Int.*, **23,** 623 (1991).
[7] D. M. P. Mingos and D. R. Baghu Orust, *Chem. Soc. Rev.*, **20,** 1 (1990).
[8] J. P. Barnier, A. Loupy, P. Pigeon, M. Ramdani, and P. Jac Quglt, *J. Chem. Soc., Perkin Trans I*, 397 (1993).
[9] G. W. Thompson, L. T. Ockerman, and J. M. Schreyer, *J. Am. Chem. Soc.*, **73,** 1379 (1951).
[10] L. Delaude and P. Laszlo, *J. Org. Chem.*, **61,** 6360 (1996).
[11] A. Mc Killop and D. W. Young, *Synthesis*, 401 and 481 (1979).
[12] M. M. Balogh and P. Laszlo, *Organic Chemistry Using Clays* (Springer Verlag, Berlin, 1993).
[13] H. M. Meshram, G. Sumithra, G. S. Reddy, Y. S. S. Ganesh, and J. S. Yadav, *Synth. Commun.* **29**(16), 2807 (1999).
[14] M. M. Heravi, D. Ajami, K. Aghapoor, and M. Ghassemzadeh, *J. Chem. Soc., Chem. Commun.*, 893 (1999).
[15] M. M. Heravi, D. Ajami, M. Ghassemzadeh, and K. Tabar-Hydar, *Synth. Commun.* **31,** 2079 (2001).
[16] B. Mohajerani, M. M. Heravi, and D. Ajami, *Monatsh. Chem.*, 2001, in press.
[17] M. M. Heravi, D. Ajami, M. M. Mojtahedi, and M. Ghassemzadeh, *Tetrahedron Lett.*, **40,** 561 (1999).